

# Preparation of copolymer of acrylamide and acrylic acid and its application for slow release sodium nitrate fertilizer

*Prof.Ass.Dr.Mohammed A.Mutar,Rafid K. Kmal*

Department of Chemistry, College of Education, University of Al-Qadissiya

## Abstract

In this search The hydrogels were prepared by free-radical crosslinking copolymerization of the monomer acrylamide (AAm) with acrylic acid (AA) as a crosslinker in aqueous solutions in the presence of potassium persulfate (KPS) as initiator and N,N,N',N'-tetramethylethylene-diamine (TEMED) as accelerator, polyacrylamide hydrogels structures were prepared by using acrylic acid (AA) (0.5, 1, 1.5, 2, 2.5) gm in the presence N,N'-methylene-bisacrylamide (MBA) as crosslinking agents at temperature 60 °c for 2 hours.

The swelling ratio (Rs) was measured for all the hydrogel structures in aqueous solution as function of time at room temperature. Sodium nitrate was loaded into polymeric matrix during in situ polymerization. The concentration of sodium nitrate released was measured on flame photometer every 1 hr. The fertilizer release studies from the sodium nitrate loaded hydrogel was studied in aqueous solution as function of time at room temperature. The results showed that the samples involving the highest release of sodium nitrate were arranged as follows:

PAAm-AA<sub>2.5gm</sub> > PAAm-AA<sub>2gm</sub> > PAAm-AA<sub>1.5gm</sub> > PAAm-AA<sub>1gm</sub> > PAAm-AA<sub>0.5gm</sub>

## 1. INTRODUCTION

Fertiliser and water are two factors which put limitations on the agricultural products<sup>(1)</sup>. Therefore, improving the utilisation of water resources and nutritive fertilisers are of a high importance. Studies show that between 40-70% of the nitrogen loaded in the fertilisers is not absorbed by the plants' roots and is permeated to the environment. This results in economical loses as well as environmental pollution. a controlled release process can solve this problem and reduce the pollution considerably. Another problem is that in most farms located in dry lands, there is a water shortage specifically in the dry seasons while they cannot take advantage from water sources in rainy seasons due to the lack of managerial skills. An appropriate solution to this problem is to use a component which can provide water and release fertiliser in a controlled way simultaneously.

Hydrogels are crosslinked polymers able to absorb and hold great amounts of water. These polymers are synthesized by using water soluble monomers through a

free radical polymerisation with the help of a suitable cross linking agent. The water absorption characteristic of hydrogels is based on its contact with a thermodynamically fitted solution and is formed by transmitting from crystalline condition to rubbery condition. This characteristic of the hydrogels has many applications in the biomedicine production<sup>(2-8)</sup>, tissue engineering technology<sup>(3)</sup>, contact lenses production<sup>(4)</sup>, and controlled release in agriculture and drug delivery systems<sup>(5,8)</sup>. Controlled release polymeric systems have many advantages in comparison with normal systems. In addition to their application in drug delivery systems, these hydrogels are used in agriculture as they reduce water consumption by reducing the numbers of irrigation<sup>(4,6)</sup>. They also reduce the plants' death due to dehydration<sup>(6-8)</sup>, stabilise fertilisers in soil, prevent active component from leaching to underground water<sup>(2,7)</sup>, and improve the plants' growth.

The substitution of controlled release method with the traditional fertilizing methods have resulted in development of the best technical solution to provide local concentration of the active agents and reduction of drain piping<sup>(1,5,8)</sup>.

Fertiliser release systems must be able to control the amount of leaving fertiliser as time goes by. Thus, amount of water inside the polymer network should be somehow controlled. Among the advantages of using hydrogels in controlled release of fertilisers in agriculture, mention can be made of:

1. As the water diffuses into the network, the loaded fertilizer exits slowly and feeds the plants' roots in a longer period of time. In addition, the amount of permeation can be controlled by changing the network structure<sup>(9)</sup>.
2. Since the interactions between the fertiliser and polymeric network are weak, a higher amount of fertiliser is released by the hydrogel in comparison with the zeolites which hold the fertiliser by adsorption<sup>(9)</sup>.

Polyacrylamide (PAAm) hydrogels and their derivatives are the subject of many studies<sup>(10, 11)</sup>. PAAm hydrogels have proven capability of water absorption and biocompatibility with physiologic body fluids. The application of PAAm hydrogels in controlled release of agrochemicals and bioactive have been investigated<sup>(12, 13)</sup>.

The present work proposes the synthesis of PAAm - based gels by a simultaneous polymerization/ crosslinking method in presence of acrylic acid (AA) as crosslinking agents. The influence of experimental parameters on both polymerization yield and swelling behavior of hydrogels and the water absorption and the release of sodium nitrate as the sample chemical fertiliser in acrylamide based hydrogels are discussed.

## **2-Experimental:-**

### **2-1. Materials**

Acrylamide (AAm, Himedia), Acrylic acid (AA, Himedia), N,N' methylene bis(acrylamide) (MBA,Fluka), Potassium peroxydisulfate (KPS, Merck), N,N,N',N'-Tetramethylene ethylene diamine (TEMED,Himedia), Sodium nitrate (Merck), Methanol (BDH),Deionized water (Iraqi Local product)

## 2-2. Apparatus

1. Digital Sensitive Balance, Sartorius AG GO TTINGEN, BL210s, GERMANY
2. Oven, TRIUP International CORP. ITALY
3. Flam Photometer, CL378, ELICOU.K, ENGLAND
4. FTIR 8400s Fourier Transform Infrared Spectro Photometer, SHIMADZU , JAPAN
5. Hot Plate STIR. BIBBY STERILINTD . UK
6. Water Still, Labtech . KOREA
7. FUME HOOD, K & K SCIENTIFIC SUPPLER , KOREA

## 2-3. Synthesis of Polyacrylamide Hydrogel

Acrylic amide (5gm) was dissolved in (50ml) de-ionized water and added (1ml) N,N,N',N'-tetramethylene-ethylene-diamine (TEMED) as accelerator , and then the solution was added into triple-necked flask , which was equipped with a stirring apparatus and a reflux condenser. The solution was stirred for 20 min and heated in a water bath of 60°C under nitrogen protection . An amount of ( 0.1gm ) potassium peroxydisulphate (KPS) as initiator dissolved in (10ml) de-ionized water , was slowly added into the flask to initiate the polymerization process after 30min. The reaction was stopped after 2h. The product was precipitated by methanol as white and solid mass.

The prepared hydrogel was poured into a petri dish 90x10 mm and was then dried in the oven of 50°C for 24h.

## 2-4. Synthesis of Acrylic Acid -Crosslinked Polyacrylamide. (A1-A5)

Acrylic amide (5gm) was dissolved in (50ml) de-ionized water and added (1ml) N,N,N',N'-tetramethylene-ethylene-diamine (TEMED) as accelerator , and then the solution was added into triple-necked flask , which was equipped with a stirring apparatus and a reflux condenser. the solution was stirred for 20 min and heated in a water bath of 60°C under nitrogen protection .then , different amounts of acrylic acid are given in table (2-1) , 0.05 gm of MBA as crosslinked agent were added into the flask . and the solution was stirred incessantly . An amount of ( 0.1gm ) potassium peroxydisulphate (KPS) as initiator dissolved in (10ml) de-ionized water , was slowly added into the flask to initiate the polymerization process after 30min. The reaction was stopped after 2h.

The prepared crosslinked hydrogel was poured into a petri dish 90x10 mm and was then dried in the oven of 50°C for 24h.

**Table (2-1). Amount of reaction parameters for synthesis of AA-crosslinked hydrogels**

Sample no.	AA.(gm) Crosslinking agent	AAm(gm) Monomer	KPS (gm) Initiator
A1	0.5	5	0.1

A2	1	5	0.1
A3	1.5	5	0.1
A4	2	5	0.1
A5	2.5	5	0.1

The prepared crosslinked hydrogel was poured into a petri dish 90×10 mm and was then dried in the oven of 50°C for 24h.

### 2-5. Fertilizer Loaded. (B1-B5)

The synthesis of loaded hydrogels is similar to that of the unloaded ones. The difference is, after complete mixing of the monomer solution, crosslinked agent acrylic acid and different amounts of fertilizer are added and mixing operation continues for another 2hrs. The fertilizer content in the obtained polymer network was (0.1, 0.2, 0.3) (gm), are given in table (2- 2).

**Table (2-2). Amount of fertilizer loaded in different amount of crosslinking agent in polyacrylamide hydrogel**

Sample no.	B1	B2	B3	B4	B5
AAM (gm) monomer	5	5	5	5	5
(AA) (gm) Crosslinking agent	0.5	1	1.5	2	2.5
Fertilizer loaded (gm)	0.1	0.1	0.1	0.1	0.1
	0.2	0.2	0.2	0.2	0.2
	0.3	0.3	0.3	0.3	0.3

### 2-6. Swelling Measurement

Dried hydrogel pieces were used to determine the degree of swelling. The swelling ratio ( $R_s$ ) was determined by immersing the hydrogels (0.1gm) of each sample in distilled water (100 ml) and was allowed to soak for 18 h at room temperature. After every one hour, they were removed from the water, blotted with filter paper to remove surface water, weighted and the swelling ratio ( $R_s$ ) was calculated using the equation below:

$$R_s = \frac{W_s - W_d}{W_d} * 100$$

where  $W_s$  and  $W_d$  are the weights of the samples swollen in water and in dry state, respectively.

### 2-7. Deswelling Measurement

the deswelling of the hydrogels was measured gravimetrically at 60 °C after wiping off the excess water from the gel surface using moistened filter paper. Before the measurement, the hydrogels were allowed to swell to equilibrium in distilled water at 25 °C. the mass changes of hydrogels were recorded at regular time intervals. Water retention (WR) is defined as follows :

$$WR = \frac{W_t - W_d}{W_s} * 100$$

Where  $W_s$  and  $W_d$  are the weight of water in the swollen gel and weight of dry gel, respectively. And  $W_t$  equals to total weight of the gel at a certain time interval

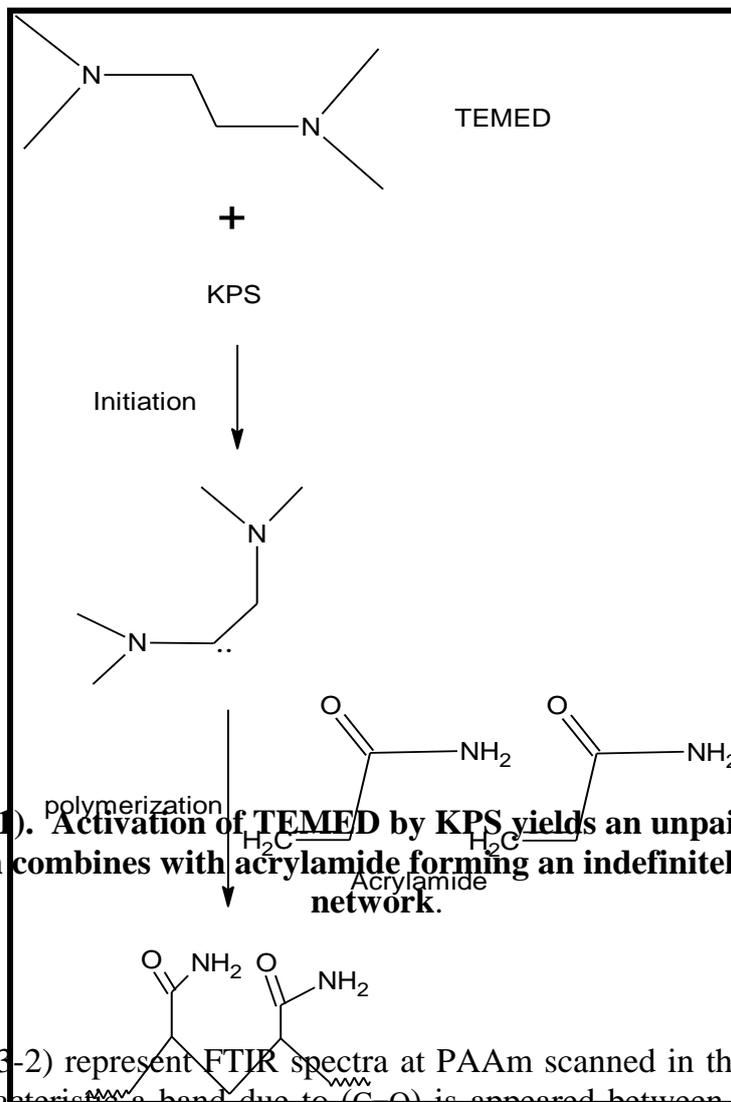
### 2-8. Fertilizer (Sodium Nitrate) Release

A loaded hydrogel sample are used in order to determine the amount of sodium nitrate released from the polymer network. The sample is dried and weighted (0.2gm) , and then immersed in 200 ml of distilled water at room temperature. The amount of sodium nitrate released was evaluated using flame photometer for one hour each 18h.

## 3-Results and Discussion

### 3-1. Synthesis of Polyacrylamide and Spectral Characterization

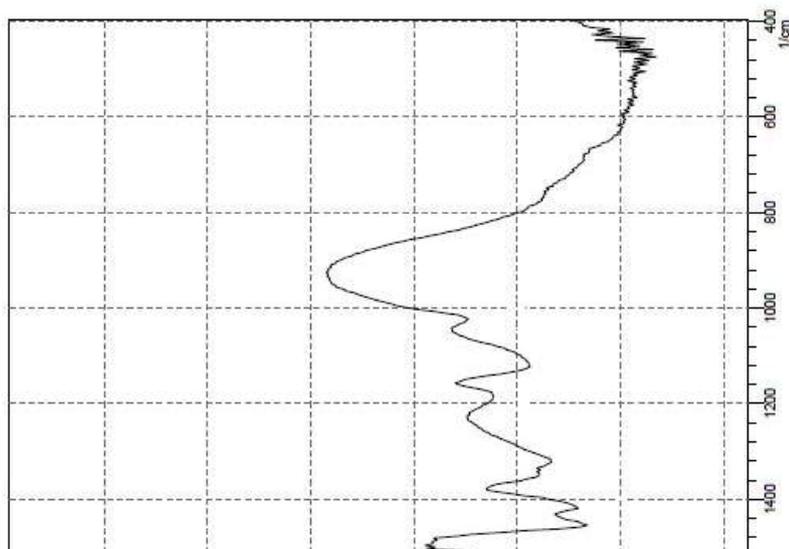
In this study, AAm hydrogels were prepared by free radical polymerization in aqueous solutions of AAm. In the polymerization process, The first step is a reaction between KPS and TEMED in which the TEMED molecule is left with an unpaired valance electron. The activated TEMED molecule can combine with an AAm. In the process the unpaired electron is transferred to the monomeric units, so that they in turn become reactive<sup>(9)</sup>. Another monomer can therefore be attached and activated in the same way. The polymer (AAm) can continue growing indefinitely, with the active center being continually shifted to the free end of the chain, see (figure 3.1). Polymerization and crosslinking process have taken 2 hours in AAm gelation in the studied conditions.



**Figure (3-1). Activation of TEMED by KPS yields an unpaired valence electron which combines with acrylamide forming an indefinitely large polymer network.**

Figures (3-2) represent FTIR spectra at PAAm scanned in the range 400-4000  $\text{cm}^{-1}$ . The characteristic band due to (C=O) is appeared between 1600-1700  $\text{cm}^{-1}$ , and the abroad absorption band due to (N-H) stretching is observed between 3200-3500  $\text{cm}^{-1}$ . The characteristic peaks (1300-1400 $\text{cm}^{-1}$ ) are due to the presence of a (C-N) vibration . The peak at around 2950  $\text{cm}^{-1}$  is due to (C-H) stretching of polymer backbone<sup>(14)</sup>.

SHIMADZU



3-2). FTIR spectra of polyacrylamide



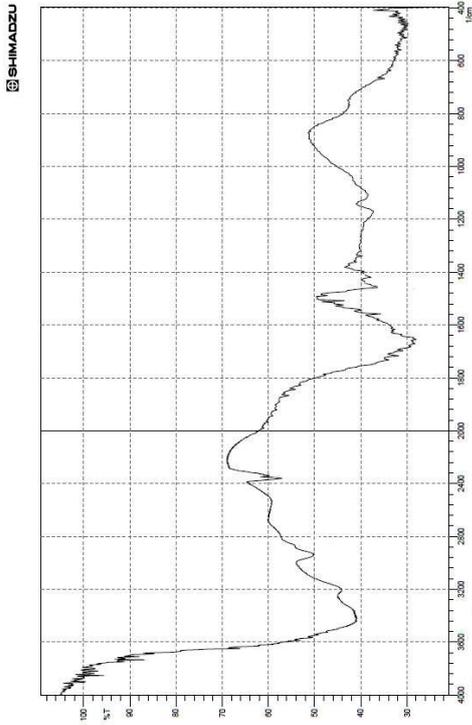


Figure (3-3). FTIR spectra of crosslinked copolymer of acrylamide and acrylic acid

### 3.

ac  
ra  
an

### Swelling

swelling ratio to time for different compositions of acrylic acid increases from 0.5 to 2.5 gm, the swelling rate increasing becomes gradually. It seems, as the acrylic acid increases within the network, a positive osmotic pressure is formed due to the presence of positive ions in the network chains (COO<sup>-</sup> group). This osmotic pressure leads to an increase in the swelling rate. Clearly, acrylic acid has a strong influence on the water sorption capacity of the copolymer hydrogels. The carboxyl groups in the acrylic acid exhibit a high capacity for holding water molecules compared to the amide of acrylamide<sup>(16)</sup>. The photographic pictures of P(AAm-AA) hydrogels are shown in figure (3-5).

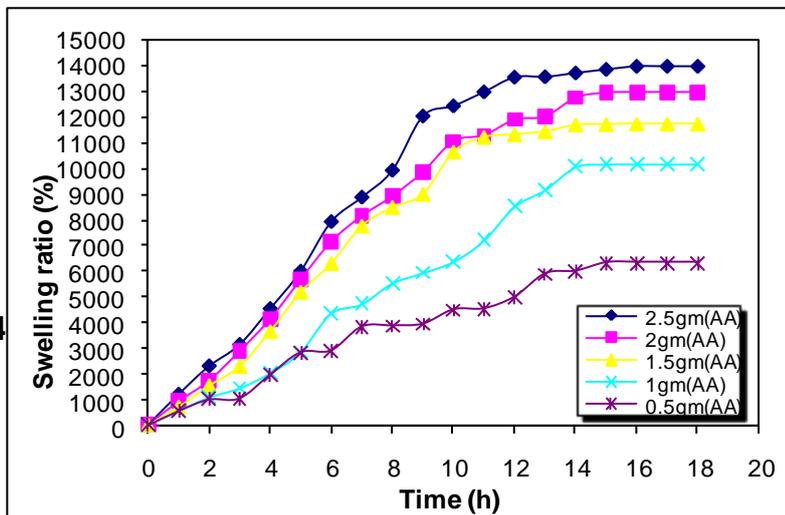
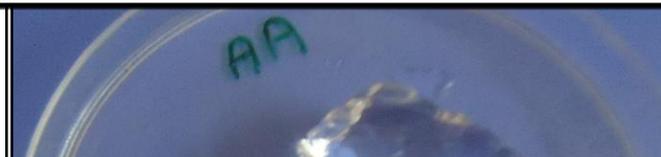


Figure (3-4)

acrylic acid.



**Figure (3-5). The photographic pictures of swelled hydrogels of P(AAm-AA)**

### **3-5. Deswelling of Hydrogels of PAAm-AA**

The deswelling of the hydrogel polymers with different AA after a temperature jump from the equilibrium swollen state at 25 °C to the hot water at 60 °C, are illustrated in figure (3-6). From figure (3-6) it can be seen that all the samples lose de-ionized water dramatically. When a hydrogel is placed in de-ionized water its shrinking immediately starts at the gel surface due to the free mobile nature of the surface and the collective diffusion of the polymer network in de-ionized water. Then a dense polymer skin layer at the surface of the gel is formed, preventing de-ionized water to flow out of the gel. As different composition was incorporated into hydrogel, the surface of the hydrogels was quite uneven compared to that of the pure PAAm hydrogel, which would weaken or destroy the dense skin layer of hydrogel. Therefore, de-ionized water molecules pass through the surface layer more easily, and the shrinking rate is improved<sup>(17)</sup>.

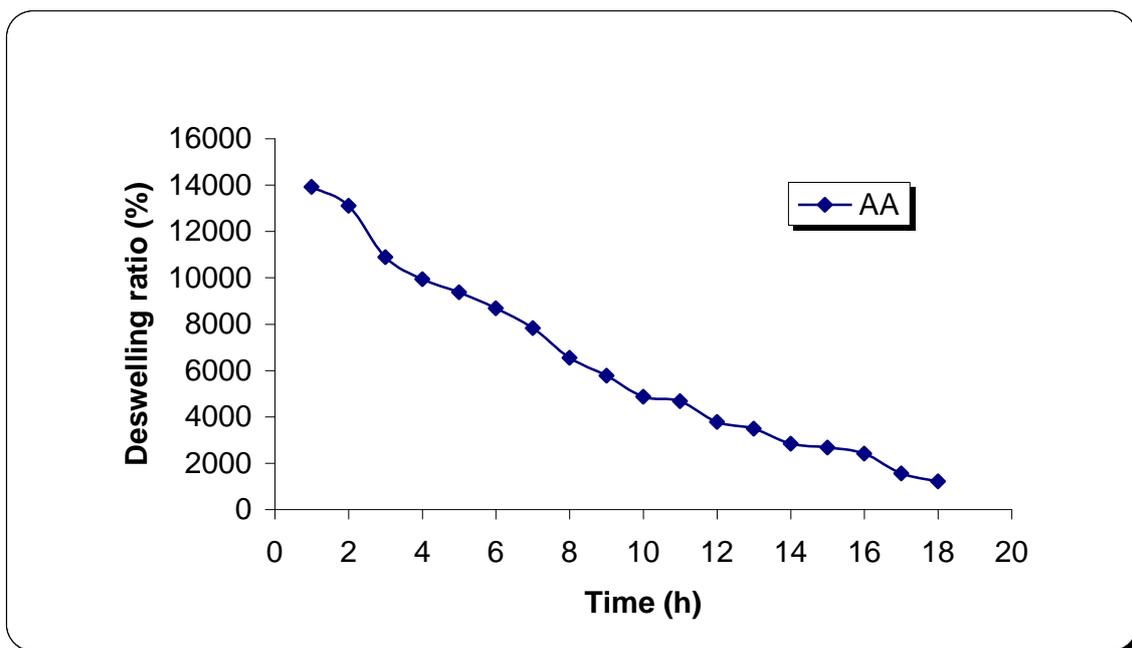
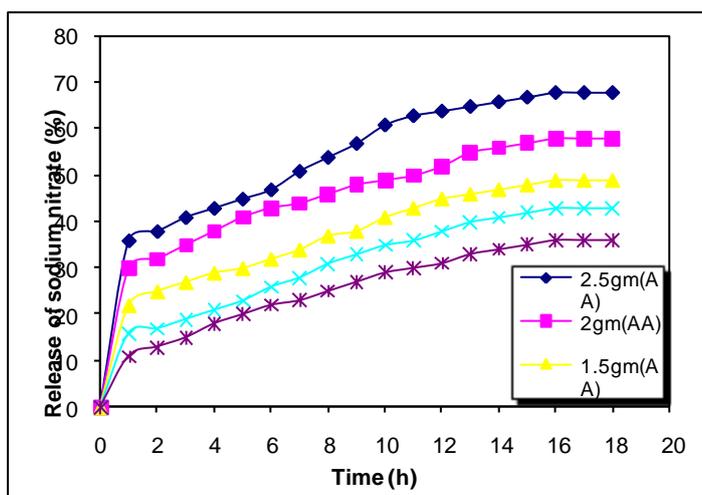


Figure (3-6). Deswelling of hydrogel of PAAm-AA at 60°C

### 3-6. Effect of AA Concentration on Release of Sodium Nitrate.

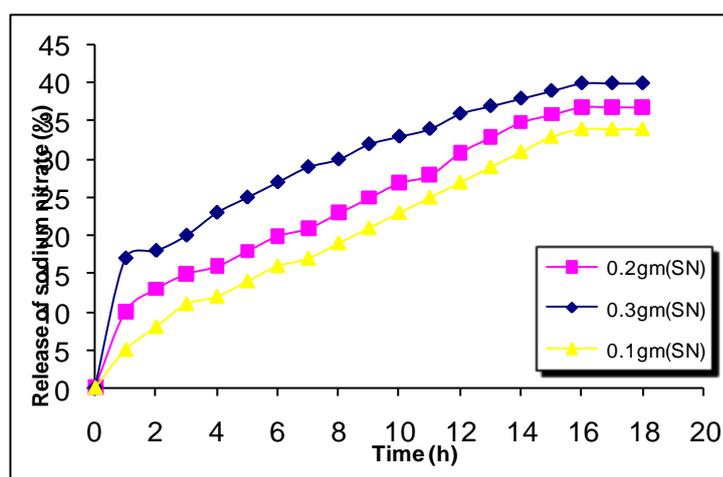
The release of sodium nitrate from PAAm hydrogels was studied by varying AA concentration. Figure (3-7) shows the effect of AA concentration on the sodium nitrate release behavior of the hydrogel. The results indicate that the release of active agent depends, obviously, on the AA concentration. As the amount of AA increases from 0.5 to 2.5 gm, the fertilizer release rate increases. The fast release of sodium nitrate is due to the higher swelling behavior of hydrogel with high concentration of AA. The high entrapment efficiency of hydrogel formulation is observed because of hydrophilicity<sup>(16,18)</sup>. It was observed that release results are very similar to swelling results:



**Figure (3-7). Effect of AA concentration of the release of sodium nitrate**

### 3-7. The Effect of Amount of Loading on Release of Sodium Nitrate.

The release profile of sodium nitrate from porous PAAm hydrogel loaded with various amounts of the sodium nitrate was studied in deionized water. The results are shown in figure (3-9). The results show that the loading is increased with increasing the sodium nitrate concentration in loading medium. The release profiles indicate that the amount of released sodium nitrate increases with increasing loading of active agent. It is attributed to the larger amount of loading. The faster the movement of the solvent front penetrating the surface of the loaded hydrogel<sup>(8)</sup>.



**Figure (3-9). Effect of percentage of loading of sodium nitrate (PAAm-AA hydrogel) on the release of sodium nitrate from hydrogel.**

## References

1. H. Kas\_göz, A. Durmus, A. Kas\_göz, Enhanced swelling and adsorption properties of AAm-AMPSNa/clay hydrogel nanocomposites for heavy metal ion removal. *Polym Adv Technol* 2008;19:213–20.
2. T. Caykara, S. Kiper, and G. Demirel, Thermosensitive poly(Nisopropyleacrylamide- co-acrylamide) hydrogels: Synthesis, swelling and interaction with ionic surfactants, *42* (2006) 348.
3. T. Caykara and A. lkay, Synthesis and network structure of ionic poly(N,N-dimethylacrylamide-co-acrylamide) hydrogels: Comparison of swelling degree with theory, *42* (2006) 1473.
4. K. Kabiri, and M.J. Zohuriaan-Mehr, Superabsorbent Hydrogel Composites, *Polym. Adv. Technol.* 14(2003) 438.
5. D. Liu, M. Sheu, C. Chen, Y. Yang, and H. Ho, Release characteristic of lidocaine from local implant of polyanionic and poly cationic hydrogels, *Journal of Controlled Release* 118 (2007) 333.
6. A. S. Hoffman, Intelligent polymers in medicine and biotechnology, *Macromol. Symp.* 98 (1995) 645.
7. Z. Li, Use of surfactant-modified zeolite as fertilizer carries to control nitrate release, *Micro porous and Mesoporous Materials* 61 (2003) 181- 188 .
8. A.K. Bajpai, Anjali Giri, Swelling dynamics of a macromolecular hydrophilic network and evaluation of its potential for controlled release of agrochemicals, *Reactive & Functional Polymers* 53 (2002) 125–141.
9. A. Hekmat, A. B. Barati, M. Zendehtel, H. R. Norouzi, A. Afraz, Synthesis and Analysis of Swelling and Controlled Release Behaviour of Anionic sIPN Acrylamide Based Hydrogels, 12th National Chemical Engineering Congress, Tbriz, Iran, 2008 .
10. D. Saraydin, E. Karadag, N. Öztop, O. Güven, Adsorption of bovine serum albumin onto acrylamidemaleic acid hydrogels. *Biomaterials*, **15**, 917–920 (1994).
11. D. Saraydin, E. Karadag, S. Cetinkaya, O. Güven, Preparation of acrylamide/maleic acid hydrogels and their biocompatibility with some biochemical parameters of human serum. *Radiation Physics and Chemistry*, **46**, 1049–1052 (1995).
12. H. A. Abd El-Rehim, Characterization and possible agricultural application of polyacrylamide/sodium alginate crosslinked hydrogels prepared by ionizing radiation. *Journal of Applied Polymer Science*, **101**, 3572–3580 (2006).
13. H. A. Abd El-Rehim, E. A. Hegazi, H. L. Abd El-Mohdy, Properties of polyacrylamide-based hydrogels prepared by electron beam irradiation for possible use as bioactive controlled delivery matrices. *Journal of Applied Polymer Science*, **98**, 1262–1270 (2005).
14. B. Stuart, *Infrared Spectroscopy: Fundamentals and Applications*. John Wiley & Sons, Ltd, 2004
15. E. Pretsch, P. Bühlmann and M. Badertscher, *Structure Determination of Organic Compounds Tables of Spectral Data*. 4<sup>th</sup> ed, Springer-Verlag Berlin Heidelberg 2009.

16. Y. Zhang, preparation of copolymers of acrylic acid and acrylamide for copper (II) capture from aqueous solution. Waterloo, Ontario, Canada, 2009.
17. Y. Dogu, O. Okay, swelling-deswelling kinetics of poly(N-isopropylacrylamide) hydrogels found in PEG solution. J of applied polymer science, 99, 37-44 (2005).
18. G.R. Mahdavinia, S.B. Mousavi, synthesis of porous poly(acrylamide) hydrogels using calcium carbonate and its application for slow release of potassium nitrate. Express polymer letters Vol.3, No.5, 279-285 (2009).

### تحضير بوليمرات مشتركة من الاكريل اميد وحامض الاكريليك وتطبيقاتها في الاطلاق البطيء لسماد نترات الصوديوم

ا.م.د.محمد علي مطر ورافد قيس كمال

قسم الكيمياء- كلية التربية- جامعة القادسية

### الخلاصة

حضرت الهلاميات المائية لمونومير الاكريلاميد بواسطة البلمرة المشتركة للجذور الحرة مع AA في المحاليل المائية بأوزان مختلفة تراوحت بين (2.5 - 0.5) غم بوجود N,N- (MBA) methylbisacrylamide كعامل تشابك وبدرجة حرارة 60 م° لمدة ساعتين . وتم قياس نسبة الانتفاخ (RS) لجميع التراكيب الهلامية في المحلول المائي كدالة للزمن في درجة حرارة الغرفة. وتم تحميل سماد نترات الصوديوم داخل البوليمر من خلال عملية البلمرة. وقد تم قياس تركيز نترات الصوديوم المتحرر باستخدام Flame photometer كل ساعة . وتم دراسة تحرر السماد من الهلاميات المائية المحملة بسماد نترات الصوديوم في المحلول المائي كدالة للزمن في درجة حرارة الغرفة ، والنتائج أظهرت ان تحرر سماد نترات الصوديوم تكون على الترتيب التالي :

PAAm-AA<sub>2.5gm</sub> > PAAm-AA<sub>2gm</sub> > PAAm-AA<sub>1.5gm</sub> > PAAm- AA<sub>1gm</sub> > PAAm-AA<sub>0.5gm</sub>